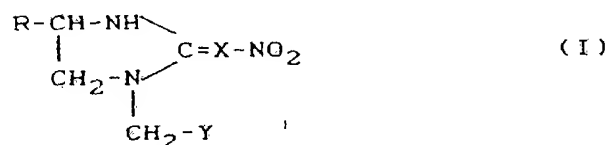




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- (56) Prior Art Documents
AU 584388 52866/86 C07D 417/06 413/06
- (57) Claim

1. An agent for use in combating keratin-digesting pests in keratin-containing textile materials, which agent is characterized in that it contains, as active substance, a combination of nitromethylene- and/or nitroimino-imidazolines on the one hand; and cyclopropanecarboxylic acid phenoxybenzyl esters or 5-phenylcarbamoyl barbituric acid derivatives or chloromethylsulphonamidodiphenyl ethers or diphenylureas or any combination thereof on the other hand; together with at least one auxiliary substance, said auxiliary substance being suitable for finishing the active substance for textile application, the agent being further characterized in that the active substance includes a compound of the formula

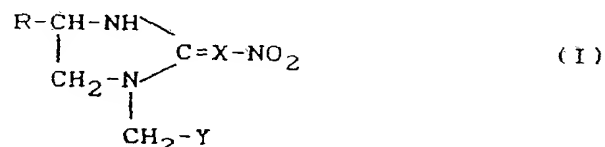


wherein

- R represents H or CH₃
X represents CH or N and
Y represents a pyridine, pyrazine or pyrimidine radical which is optionally substituted by halogen or C₁-C₄-alkyl.

3. A process for the treatment of keratin-containing textile materials for protection from infestation and ingestion damage by keratin digesting pests, characterized in that there is used, in carrying out such treatment, an agent according to either one of claims 1 or 2.

4. A process for the treatment of keratin-containing textile materials for protection from infestation and ingestion damage by keratin-digesting pests characterized in that there is used, in carrying out such treatment, an agent that contains a nitromethylene and/or nitroiminoimidazoline as active substance, together with at least one auxiliary substance suitable for finishing the active substance for textile application, the agent in turn being further characterized in that the active substance includes a compound of the formula



wherein

- R represents H or CH₃,
X represents CH or N and
Y represents a pyridine, pyrazine or pyrimidine radical which is optionally substituted by halogen or C₁-C₄-alkyl.

5. A process according to claim 4 characterized in that the compound is

Our Ref: 309959

633883

AUSTRALIA
Patents Act

FORM 10

COMPLETE SPECIFICATION

(ORIGINAL)

Application Number:
Lodged:

Complete Specification Lodged:
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Published:

Priority:
Related Art:

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Complete specification for the invention entitled
"Agents against keratin pests."

The following statement is a full description of this invention, including the best method of performing it known to me:-

5

Agents against keratin pests

10 The invention relates to an agent for combating
moths and other keratin-digesting textile pests, which
is based on nitromethylene- or nitroiminoimidazolines
and mixtures thereof, with cyclopropanecarboxylic acid
phenoxybenzyl esters, 5-phenylcarbamoyl barbituric acid
derivatives, chloromethylsulphonamidodiphenyl ethers
and/or diphenylureas.

15 It is known that this group of substances has
insecticidal properties and is therefore recommended in
particular for use in the agricultural sector (compare
DE-A-2,514,402 and EP-A-192,060 = US-A-4,747,060).

20 It is also known that cyclopropanecarboxylic acid
phenoxybenzyl esters of the most diverse forms have
powerful insecticidal properties (cf. for example GB A
1,413,491 and DE-A 2,709,264), that 5-phenylcarbamoyl
barbituric acid compounds have insecticidal properties
(cf. CH-A 653,840 and EP-A 0,169,168), that chloro-
25 aminodiphenyl ethers e.g. 4,5,2',4',4''-pentachloro-2-
chloromethylsulphenamidodiphenyl ether, have an
ingestion-inhibiting action against keratin-digesting
pests, when applied to textiles (cf. EP-A 311,851) and
that diphenylureas of a specific composition also have
30 an ingestion-inhibiting action against keratin-digesting
pests, when applied to textiles (cf. EP 0,318,431 A2).

35 It has now been found that these substances also
have an excellent ingestion-preventing action against
moths and other keratin-digesting insects when they are
used under the conditions of the textile industry in
combination with finishing auxiliaries customary in this
branch.

Le A 26 717-Foreign Countries

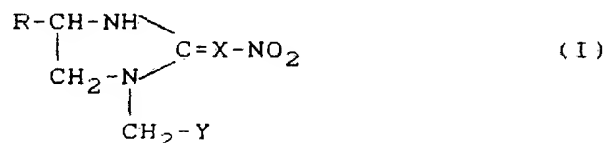
This effect is to be regarded as surprising, since insecticides which are used as spraying agents in the agricultural sector can in no way generally also be used for preventing damage to textiles by the keratin pests of specialized digestion.

It is furthermore remarkable that the agents according to the invention have a higher activity than comparable known protecting agents.

The significantly more advantageous eco-toxicological properties, especially in respect of toxicity to fish, of the compounds according to the invention in comparison with the agents known from the prior art must also be emphasised.

Finally it must be considered particularly surprising that mixtures of compounds I-V display a marked synergistic action in combating keratin pests, compared with the individual components.

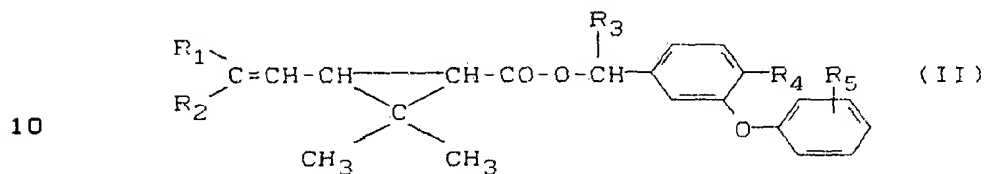
Agents which are preferably to be employed correspond to the formula



wherein

- R represents H or CH₃,
X represents CH or N and
Y represents a pyridine, pyrazine or pyrimidine radical which is optionally substituted by halogen or C₁-C₄-alkyl.

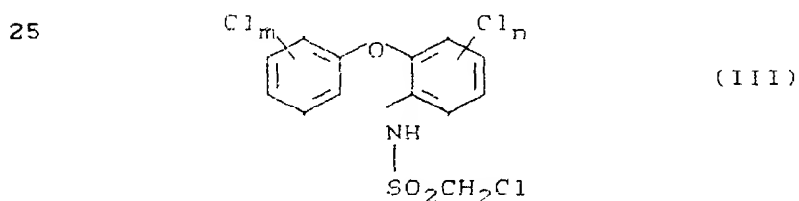
Where cyclopropanecarboxylic acid phenoxybenzyl
 5 esters are used, those of the formula



in which

- 15 R_1 represents hydrogen, alkyl or halogen
 R_2 represents alkyl, halogen or phenyl which is
 optionally substituted by halogen,
 R_3 represents hydrogen, cyano or ethinyl,
 R_4 represents hydrogen or halogen and
 20 R_5 represents hydrogen or halogen,
 are preferred.

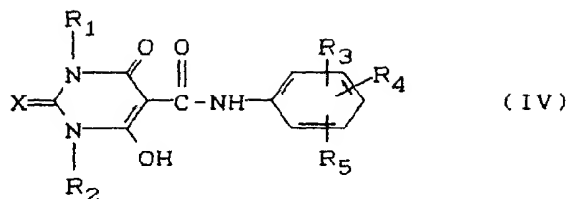
Of the chloromethylsulphonamidodiphenyl ethers,
 those of the formula



30 in which the sum of m and n is 4-7, are preferably
 employed.

Where 5-phenylcarbamoylbarbituric acid derivatives
 are used as an additional component, those of the
 35 formula

5



10

are preferably used. In this formula

X is oxygen or sulphur,

R₁ and R₂ are in each case alkyl having 3 or 4 C atoms,
alkenyl having 3 or 4 C atoms, benzyl or
optionally substituted phenyl,

15

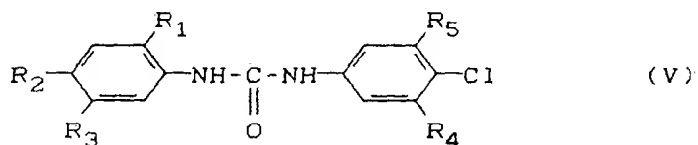
R₃ is halogen, nitro or C(halogen)₃,

R₄ is hydrogen, halogen or C(halogen)₃ and

R₅ is hydrogen, halogen, methyl or methoxy.

If diphenylureas are used, those of the formula

20



25

wherein

R₁ denotes hydrogen or 4-chlorophenoxy-6-sulphonate,

R₂ denotes hydrogen or chlorine,

30

R₃ denotes hydrogen or trifluoromethyl,

R₄ denotes hydrogen or chlorine and

R₅ denotes hydrogen or trifluoromethyl.

35

are preferably used.

5 "Halogen" here is understood as meaning, in particular, fluorine and - above all - chlorine.

The preferred alkyl radical is the methyl group.

Compounds of the formula (I) in which X = N and Y denotes a chloropyridine radical are particularly
10 preferred,

The substances per se - as already mentioned - are known and are described in detail in EP-A-192,060.

The finishing of these substances for textile application is also carried out by known methods by
15 means of customary auxiliaries, such as, for example, emulsifiers, water-miscible organic solvents, standardizing agents, antifreeze agents and the like for a liquid finish.

The keratin pests include
20 from the order of the Tineidae (true moths) for example *Tineola bisselliella* (clothes moth),
Tinea pellionella (fur moth) and
Hofmannophila pseudospretella (seed moth)
and from the series of beetles the larvae of two genera
25 of Dermestidae (bacon beetle), for example
Anthrenus verbasci (mullen blossom beetle),
Anthrenus pimpinellae (pimpernel blossom beetle),
Anthrenus scrophulariae (common carpet beetle),
30 *Anthrenus fasciatus* (ribboned carpet beetle),
Attagenus pello (spotted fur beetle),
Attagenus piceus (dark fur beetle).

35

5 The protective substances according to the invention can be used in various ways, for example in powder form for cleaning furs and skins, in a powder blend for repelling or destroying pests, or in the form of emulsions or dispersions from an aqueous liquor or from organic solvents by the method of drycleaning.

10 They can be used in practically all the states of processing and all the wet application and spraying processes customary in the textile industry, if appropriate together with other finishing processes, on wool, woollen textiles and wool-containing textiles as well
15 as feathers, hair and related material or material produced therefrom.

 The agent can be added, for example, to the dyebath before the customary dyeing process, but it can also be applied during washing of wool. The treatment is pre-
20 ferably carried out in an aqueous medium.

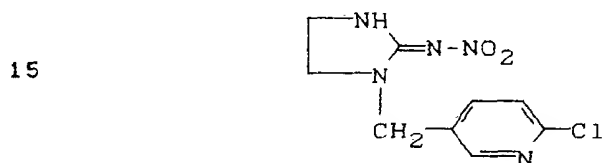
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Example 1

- 5 Wool, woollen yarn or a sheet-like structure of
wool is introduced at 40°C in a liquor ratio of 10:1
into a treatment bath containing, per litre of water,
3 g of acetic acid (60% strength),
5 g of calcined sodium sulphate,
10 1.5 g of an addition product of stearyl-methylethanol-
amine and 40 mol of ethylene oxide,
0.025 g of the compound of the formula



and

- 20 2 g of Acid Yellow 151 (= C.J. 13 906)

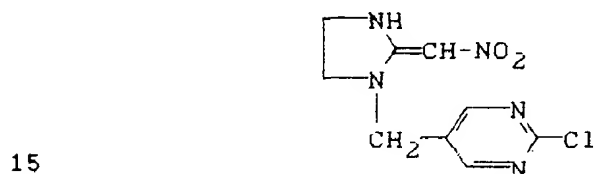
25 The bath is then heated to the boiling point and
the dyeing is finished in the customary manner. The
yellow-dyed woollen material has good protection from
being eaten by moths and beetles.

Example 2

- 30 Carpet yarn which consists of a wool/polyamide
mixture in a ratio of 80:20 is introduced at 40°C in a
liquor ratio of 25:1 into a treatment bath which con-
tains, per litre of water,

35

- 0.4 g of acetic acid (60% strength),
5 1.2 g of ammonium sulphate,
0.6 g of a condensation product of phenylsulphonic
acid, dihydroxydiphenyl sulphone and formaldehyde,
0.8 g of an addition product of stearyl-methylethanol-
amine and 40 mol of ethylene oxide,
10 0.1 g of the compound of the formula



and

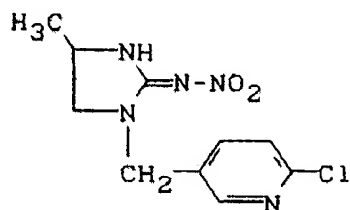
- 1.5 g Acid Yellow 151 (= C.J. 13 906)
20

The mixture is then heated to the boiling point and the dyeing is finished in the customary manner. The yellow-dyed woollen content of the carpet yarn has good protection from being eaten by moths and beetles.

- 25 Good results are also obtained if a treatment bath which contains, per litre of water,
0.4 g of acetic acid (60% strength),
1.2 g of ammonium sulphate,
1.2 g of ®EDOLAN PAW fl.,
30 0.4 g of ®AVOLAN S,
0.6 g of Acid Yellow 49 (=C.I. 18 640) and the above-mentioned amounts of the compound of the formula

35

5



is used.

10

Example 3

500 kg of carpet yarn consisting of wool or a wool mixture, preferably with polyamide in a ratio of 80:20, are washed and treated per hour by the continuous washing process on a washing unit customary in industry.

For this, in the last tank of the washing unit the liquor is brought to a pH of below 7 with dilute acetic acid and 0.05 g per litre of the active substance mentioned in Example 1 is added.

The treatment is carried out at 50°C.

To maintain the active compound concentration in the treatment bath, the bath is topped up with 125 g of the abovementioned compound.

This topping up is performed by continuous addition of an aqueous solution to the bath throughout the entire treatment time. The carpet yarn treated in this way has good protection from being eaten by moths and beetles. This also applies to the final article produced therefrom.

35

Example 4

5 1,000 kg of raw wool are washed and treated per
hour by the continuous washing process in a Leviathan
or a comparable unit (for example Mini-Bowl).

For this, in the last tank of the Leviathan the
liquor is brought to a pH of below 7 with dilute acetic
10 acid and
0.05 g per litre of a compound according to Example 1
is added.

The treatment is carried out at 70°C.

To maintain the active compound concentration in
15 the treatment bath, the bath is topped up with 250 g of
the abovementioned compound.

This topping up is performed by continuous addition
of an aqueous solution to the bath throughout the entire
treatment time. The raw wool treated in this way has
20 good protection from being eaten by moths and beetles.
The wool can be passed to all the further processing
processes customary in the textile industry.

Example 5

5,000 kg of raw wool are treated by the spray pro-
25 cess during mixing in preparation for spinning. The
spray application here is an integrated constituent of
the spinning oil in accordance with the following recom-
mended recipe.

Total application	625 l,
30 containing	75 l of a spinning oil (®Solfil 591)
	1,250 g of the active sub- stance according to Example 1
35	the remainder being water.

The raw wool treated in this way has a good protection from being eaten by moths and beetles. The wool can be passed to all the further processing processes customary in the textile industry.

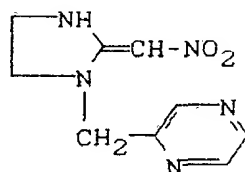
Example 6

Wool, woollen yarn or a sheet-like structure of wool is introduced at 20 to 40°C in a liquor ratio of 10:1 into a treatment bath which contains, per litre of water,

3 g of acetic acid (60% strength),

1 g of an ammonium salt of a C₁₂-C₁₄-alkylsulphonate mixture and

0.025 g of the compound of the formula



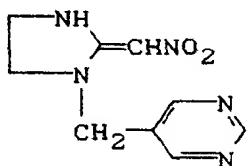
The treatment bath is then heated to 60°C and left at this temperature.

The woollen material treated in this way has a good protection from being eaten by moths and beetles.

Example 7

Carpet goods which contain 2,000 g/m² in the pile and have a backing which consists of polypropylene or jute is sprayed with a solution which contains, per litre of water and at a spray application of 20% of the weight of the goods

1 g of an ammonium salt of C₁₂-C₁₄-alkylsulphonate
mixture and
1.25 g of the compound of the formula



The spray application is performed uniformly over the entire width of the goods, it being necessary for the spray cones to overlap slightly. The goods are then passed to the drier.

The carpet goods treated in this way have good protection from being eaten by moths and beetles in the entire pile material, both on the pile surface and within the depth of the pile.

Example 8

Carpet goods which contain 2,000 g/m² in the pile and have a backing consisting of polypropylene or jute are treated by the foam application process. The foam application can be performed here in accordance with the following system:

Speed	4 m/minute
Wet application	30%
Foaming	1:50
Cushion pressure	0.4 bar.

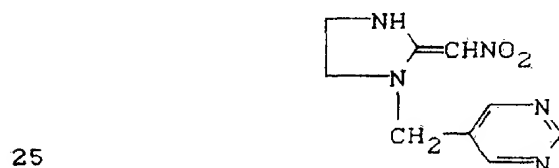
5 The liquor to be foamed contains, per litre of
water,
5 g of dodecyloxyethyl-dihydroxyethyl-amine oxide and
0.85 g of the active substance of Example 7.

The penetration into the depth of the pile is good,
without the moisture entering the backing. The carpet
10 goods treated in this way have a good protection from
being eaten by moths and beetles both on the pile
surface and in the depth of the pile.

Example 9

15 Woollen piece goods weighing 500 g/m² are treated
on a padder so that a liquor pick-up of 100%, based on
the weight of the goods, results.

The liquor contains, per litre of water,
2 g of an ammonium salt of a C₁₂-C₁₄-alkylsulphonate
mixture and
20 0.25 g of the compound of the formula



The goods are passed from the padder into the drier
or stenter.

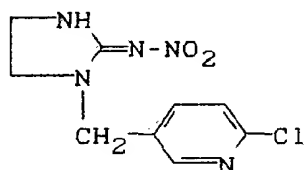
30 The piece goods treated in this way have good pro-
tection from being eaten by moths and beetles.

35

Example 10

- 5 Wool, woollen yarn or a sheet-like structure of wool is introduced at 40°C in a liquor ratio of 10:1 into a treatment bath containing, per litre of water,
3 g of acetic acid (60% strength),
5 g of calcined sodium sulphate,
10 1.5 g of an addition product of stearyl-methylethanolamine and 40 mol of ethylene oxide,
0.25 mg of the compound of the formula

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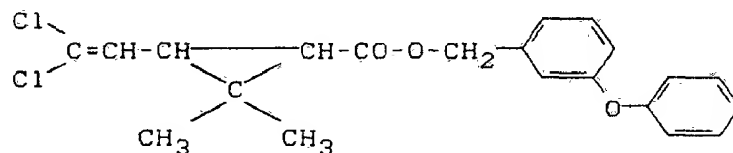


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and

0,75 mg of the compound of the formula

25



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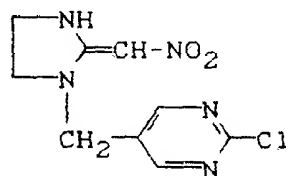
and

2 g of Acid Yellow 151 (=C.I. 13 906).

- The bath is then heated to the boiling point and the dyeing is finished in the customary manner. The
35 yellow-dyed woollen material has good protection from being eaten by moths and beetles.

Example 11

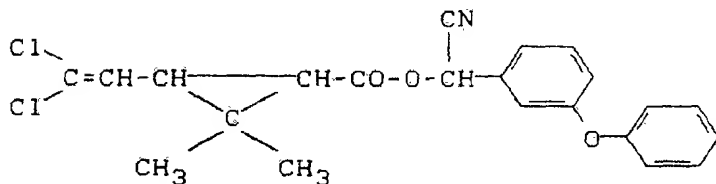
- 5 Carpet yarn which consists of a wool/polyamide mixture in a ratio of 80:20 is introduced at 40°C in a liquor ratio of 25:1 into a treatment bath which contains, per litre of water,
- 0.4 g of acetic acid (60% strength),
- 10 1.2 g of ammonium sulphate,
- 0.6 g of a condensation product of phenylsulphonic acid, dihydroxydiphenyl sulphone and formaldehyde,
- 0.8 g of an addition product of stearyl-methylethanolamine and 40 mol of ethylene oxide,
- 15 0.25 mg of the compound of the formula



20

and

- 25 0.75 mg of the compound of the formula



30

and

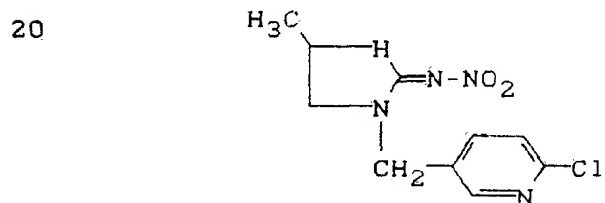
- 35 1.5 g Acid Yellow 151 (= C.J. 13 906).

5 The mixture is then heated to the boiling point and the dyeing is finished in the customary manner. The yellow-dyed woollen content of the carpet yarn has good protection from being eaten by moths and beetles.

Example 12

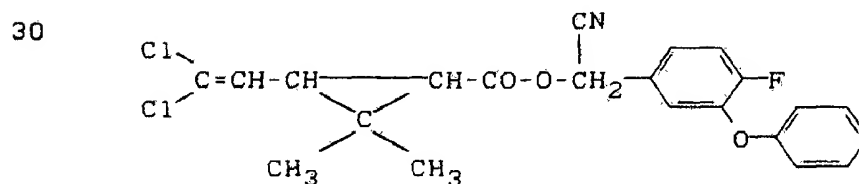
10 500 kg of carpet yarn consisting of wool or a wool mixture, preferably with polyamide in a ratio of 80:20, are washed and treated per hour by the continuous washing process on a washing unit customary in industry.

15 For this, in the last tank of the washing unit the liquor is brought to a pH of below 7 with dilute acetic acid and 0.5 mg per litre of the compound of the formula (A)



25 and

1.5 mg per litre of the compound of the formula (B)



35 are added.

The treatment is carried out at 50°C.

5 To maintain the active compound concentration in the treatment bath, the bath is topped up with 1.25 g of the abovementioned compound of the formula (A)

and

10 3.75 g of the abovementioned compound of the formula (B).

This topping up is performed by continuous addition of an aqueous solution to the bath throughout the entire treatment time. The carpet yarn treated in this way has good protection from being eaten by moths and beetles. This also applies to the final article produced therefrom.

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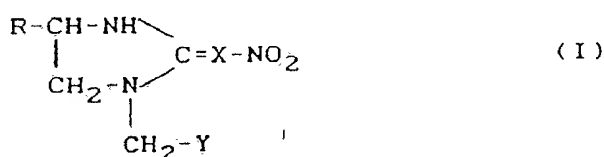
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The claims defining the invention are as follows:

1. An agent for use in combating keratin-digesting pests in keratin-containing textile materials, which agent is characterized in that it contains, as active substance, a combination of nitromethylene- and/or nitroimino-imidazolines on the one hand; and cyclopropanecarboxylic acid phenoxybenzyl esters or 5-phenylcarbamoyl barbituric acid derivatives or chloromethylsulphonamidodiphenyl ethers or diphenylureas or any combination thereof on the other hand; together with at least one auxiliary substance, said auxiliary substance being suitable for finishing the active substance for textile application, the agent being further characterized in that the active substance includes a compound of the formula



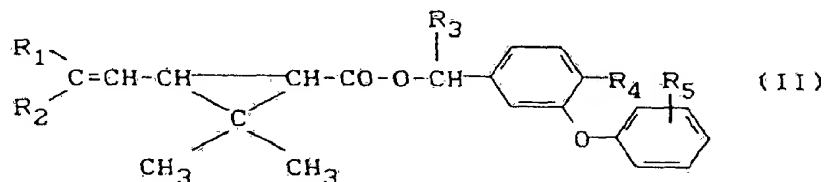
wherein

R represents H or CH₃

X represents CH or N and

Y represents a pyridine, pyrazine or pyrimidine radical which is optionally substituted by halogen or C₁-C₄-alkyl.

2. An agent according to claim 1 in which the active substance also includes at least one compound of the formula



in which

R₁ represents hydrogen, alkyl or halogen

R₂ represents alkyl, halogen, or phenyl which is optionally substituted by halogen,

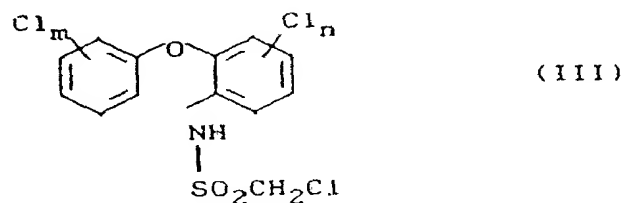
R₃ represents hydrogen, cyano or ethinyl,

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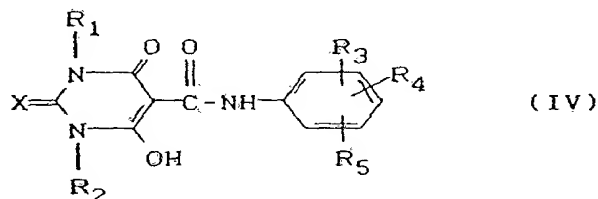


R_4 represents hydrogen or halogen and
 R_5 represents hydrogen or halogen,

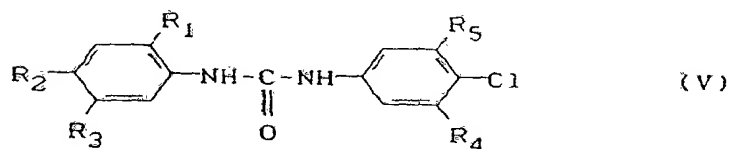
or



in which
the sum of m and n is 4-7,
or



in which
X denotes oxygen or sulphur,
 R_1 and R_2 in each case denote alkyl having 3 or 4 C atoms, alkenyl having 3 or 4 C atoms, benzyl or optionally substituted phenyl,
 R_3 denotes halogen, nitro or $C(\text{halogen})_3$,
 R_4 denotes hydrogen, halogen or $C(\text{halogen})_3$ and
 R_5 denotes hydrogen, halogen, methyl or methoxy
or



wherein

R₁ denotes hydrogen or 4-chlorophenoxy-6-sulphonate,

R₂ denotes hydrogen or chlorine

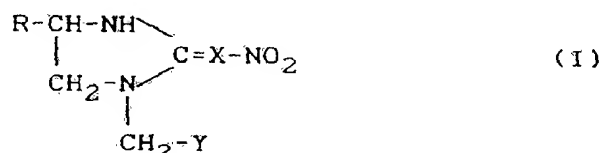
R₃ denotes hydrogen or trifluoromethyl,

R₄ denotes hydrogen or chlorine and

R₅ denotes hydrogen or trifluoromethyl.

3. A process for the treatment of keratin-containing textile materials for protection from infestation and ingestion damage by keratin digesting pests, characterized in that there is used, in carrying out such treatment, an agent according to either one of claims 1 or 2.

4. A process for the treatment of keratin-containing textile materials for protection from infestation and ingestion damage by keratin-digesting pests characterized in that there is used, in carrying out such treatment, an agent that contains a nitromethylene and/or nitroiminoimidazoline as active substance, together with at least one auxiliary substance suitable for finishing the active substance for textile application, the agent in turn being further characterized in that the active substance includes a compound of the formula



wherein

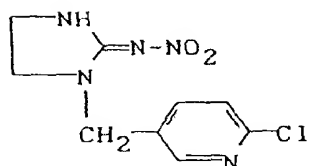
R represents H or CH₃,

X represents CH or N and

Y represents a pyridine, pyrazine or pyrimidine radical which is optionally substituted by halogen or C₁-C₄-alkyl.

5. A process according to claim 4 characterized in that the compound is





6. A process according to any one of claims 3 to 5, characterized in that the treatment is carried out in an aqueous medium.

DATED this 16th day of October, 1992.

BAYER AKTIENGESELLSCHAFT
By Its Patent Attorneys
DAVIES COLLISON CAVE



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